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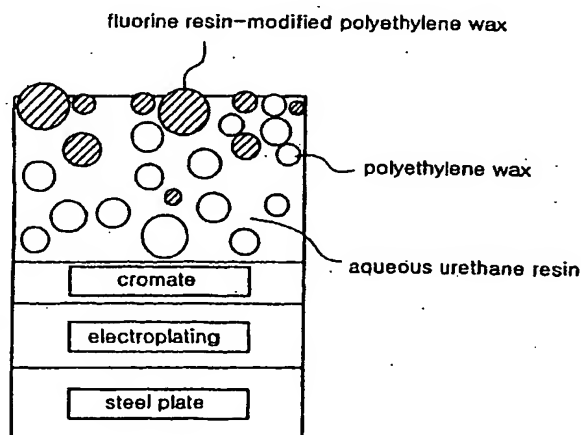
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ning of each regular issue of the PCT Gazette.

(54) Title: PREPARATION OF AQUEOUS URETHANE RESIN COMPOSITION



(57) Abstract: Disclosed are a method for preparing an aqueous urethane resin composition, a method for preparing an aqueous lubricant urethane resin composition, and a surface treatment method of steel plates. The aqueous urethane resin composition is prepared by reacting polyester polyol, diisocyanate, dimethyl propionic acid or dimethyl butyric acid, and amine to give a prepolymer, dispersing the prepolymer in water, introducing into the water-dispersed prepolymer a chain extender, and adding the aqueous polyurethane resin solution with a curing agent. The dimethyl propionic acid or dimethyl butyric acid serves as a hydrophilic moiety for water dispersion. The aqueous lubricant urethane resin composition is prepared from the aqueous urethane resin composition in combination with a wax mixture of fluorine resin-modified polyethylene wax and polyethylene wax, colloidal silica and a coupling agent. This lubricant resin composition is coated at a thickness of 0.5-5.0 (μm) on a chromated, electroplated steel plate which is then baked at 110-200 (°C) and quenched in water. In addition to being superior in thin coatability, corrosion resistance, film flexibility, plate-adhesion property, surface friction, chemical resistance, and overcoatability, the lubricant resin composition shows excellent compatibility with various usually used additives.

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Preparation of aqueous urethane resin composition

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BACKGROUND OF THE INVENTION

1. Field of the invention

The present invention relates to a method for preparing an aqueous urethane resin composition suitable as a binder resin solution for coating steel plates, a method for preparing an aqueous lubricant urethane resin composition, and use of such compositions. More particularly, the present invention relates to a method for preparing an aqueous urethane resin composition superior in various physical properties, including corrosion resistance, paint adhesion, chemical resistance, processability, and surface friction properties and suitable as a binder resin for coating functional steel plates. Also, the present invention is concerned with an aqueous lubricant urethane resin composition containing the aqueous urethane resin, which can give a great contribution to improving the steel plate in corrosion resistance, chemical resistance, deep drawability, post-processing appearance, and surface friction properties as well as enables the steel plate to be processed into products under an oil-less condition. Further, the present invention relates to surface treatment of chromated, electroplated steel plates.

2. Description of the Prior Art

To be useful for thin film coating, an aqueous resin is required to possess excellent corrosion resistance, coating flexibility in terms of

processability, adhesiveness to steel plates, surface friction characteristics, chemical resistance, and overcoatability as well as to be used in general uses.

Until recent, there have been developed various coating resins for steel plates of solvent types or aqueous types. In regard to a functional steel plate, a conventional coating resin can be referred to Japanese, Pat. Laid-Open Publication No. Hei. 5-138120. In this reference patent, bisphenol type epoxy resins, multi-
10 functional epoxy resins, alkyd resins, ester resins, acryl resins, urethane resins, and modified derivatives thereof are mentioned along with curing agents such as various amine compounds, amino resins, and isocyanate compounds. However, they are not described in detail,
15 but enumerated simply. Further, their use ranges are too wide to discriminate resin properties.

Surface treatment techniques, in which chromated, electroplated steel plates are coated with various resin thin films to serve various purposes, are well known in
20 the art. Japanese Pat. Laid-Open Publication Nos. Hei. 5-138120, 4-44840, 3-71836, 3-39485, 3-16726, and 3-270932 disclose lubricant solutions for steel plates. However, nowhere are in detail mentioned a blackening phenomenon in processed parts after deep drawing and base
25 resins of the resinous solutions.

Japanese Pat. Laid-Open Publication No. Hei. 5-3052668 discloses use of a urethane resin in forming a non-continuous coat--highly resistant to--corrosion. A simple combination of a fluorine compound and
30 polyethylene is used as a lubricant and applied to a steel plate by use of an electrostatic method. However, an electrostatic method results in non-continuous films

which are unfavorable in terms of corrosion resistance.

Korean Pat. Appl'n. Nos. 96-39091 and 97-73554 describe polyethylene waxes modified with fluorine resins with an application for steel plates resistant to fingerprinting. Since such fingerprinting-resistant steel plates are usually developed to undergo low machining techniques such as bending and drilling, a problem occurs when deep drawing techniques are applied to them.

Korean Pat. Appl'n. No. 97-73554 discloses a silica-modified ethylene-acryl resin for coating fingerprinting-resistant steel plates. This resin is superb in workability, solution stability, physical properties such as storage properties, and chemical resistance, but poor in processability when its flexibility is taken into account.

Lubricant resin-coated steel plates are preferably processed without using oils. When contaminants have to be removed during or after processing, a lubricant resin solution superior in chemical resistance such as alkali resistance and solvent resistance is applied in order to prevent the resin coating from being damaged.

There is an increasing demand to provide chemical resistance and blackening resistance for computer parts and transparent household appliance parts. Thus, it is required to permanently keep surfaces clean after processing.

SUMMARY OF THE INVENTION

Therefore, it is an object of the present invention to provide a method for preparing an aqueous urethane

resin composition which is able to be thinly coated onto steel plates and superior in fingerprinting-resistance, overcoatability and corrosion resistance with excellent compatibility with other additives.

5 It is another object of the present invention to provide a method for preparing an aqueous lubricant urethane resin composition which is characterized by oil-less deep drawing properties, process-defective reduction, blackening improvement, and chemical resistance.

10 It is a further object of the present invention to provide a surface treatment method of chromated, electroplated steel plates using such an aqueous lubricant urethane resin composition.

In accordance with a first embodiment of the present invention, there is provided a method for preparing an aqueous urethane resin composition, comprising the steps of: (1) producing an aqueous polyurethane resin solution by (a) reacting 100-150 parts by weight polyester polyol, 30-50 parts by weight diisocyanate, 5-15 parts by weight dimethyl propionic acid or dimethyl butyric acid, and 3-10 parts by weight amine at 55-85 °C for 5-6 hours to give a prepolymer ranging, in NCO radical content, from 2 to 8%, said dimethyl propionic acid or dimethyl butyric acid serving as a hydrophilic moiety for water dispersion; (b) dispersing the prepolymer at 30-40 °C in water; and (c) introducing into the water-dispersed prepolymer a chain extender selected from the group consisting of glycol, triol and diamine at 25-30 °C in such a way that the reaction mole ratio between said chain extender and NCO residues is controlled to give the final product with a molecular weight of 30,000-100,000; (2) adding the

aqueous polyurethane resin solution with block isocyan type or aziridine type curing agent at an amount of 3-15 % by weight based on the weight of the resin solid content.

- 5 In accordance with a second embodiment of the present invention, there is provided a method for preparing an aqueous lubricant urethane resin composition, comprising the steps of: (1) producing an aqueous polyurethane resin solution by (a) reacting 100-150 parts
10 by weight polyester polyol, 30-50 parts by weight diisocyanate, 5-15 parts by weight dimethyl propionic acid or dimethyl butyric acid, and 3-10 parts by weight amine at 55-85 °C for 5-6 hours to give prepolymer ranging, in NCO radical content, from 2 to 8%, said
15 dimethyl propionic acid or dimethyl butyric acid serving as a hydrophilic moiety for water dispersion; (b) dispersing the prepolymer at 30-40 °C in water; and (c) introducing into the water-dispersed prepolymer chain extender selected from the group consisting of glycol,
20 triol and diamine at 25-30 °C in such a way that the reaction mole ratio between said chain extender and NCO residues is controlled to give the final product with a molecular weight of 30,000-100,000; (2) adding the aqueous polyurethane resin solution with block isocyan
25 type or an aziridine type curing agent at an amount of 3-15 % by weight based on the weight of the resin solid content; (3) adding a mixture comprising a fluorine resin-modified polyethylene and a polyethylene wax at a ratio of 1:0.3-1:0.7 to the resin solution at an amount
30 of 5-30 % by weight based on the weight of the resin solid content, said fluorine resin-modified polyethylene wax ranging, in specific gravity, from 0.98 to 1.02 with

a particle size of 0.1-1.5 μm , said polyethylene wax ranging, in molecular weight, from 1,500 to 3,000 with a particle size of 0.05-1.0 μm ; (4) adding a colloidal silica in the resin solution obtained in the step (3) at an amount of 10-30 % by weight based on the weight of resin solid content; (5) adding in the resin solution obtained in the step (4) a coupling agent selected from the group consisting of silane coupling agents containing an epoxy group, an amine group, and/or an acryl group and titanium coupling agents containing phosphorus and/or an amine group at an amount of 0.1-0.5 % by weight based on the total weight of the resin solid content; and (6) diluting the resin solution with pure water into a final resin solid content of 10-30 % by weight.

In accordance with the third embodiment of the present invention, there is provided a surface treatment of chromated, electroplated steel plates, comprising the steps of: coating, on an zinc-electroplated steel plate chromated at a chrome amount of 4-200 mg/m^2 , the aqueous lubricant urethane resin composition at a dry coating thickness of 0.5-5.0 μm , baking the steel plate at a steel temperature of 110-200 $^{\circ}\text{C}$, and quenching the steel in water.

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BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a schematic cross section showing a steel plate coated with the aqueous lubricant urethane resin composition of the present invention.

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DETAILED DESCRIPTION OF THE PRESENT INVENTION

The present invention contemplates a method for preparing an aqueous urethane resin composition. The aqueous urethane resin composition according to the present invention can be coated on steel plates to a thickness as thin as 0.3-0.7 μm . In addition to being superior in thin coatability, corrosion resistance, film flexibility, plate-adhesion property, surface friction, chemical resistance, and overcoatability, the aqueous urethane resin composition shows excellent compatibility with various additives which are usually used in plate steel coating compositions.

The aqueous urethane resin composition of the present invention is prepared by preparing a urethane prepolymer, dispersing the prepolymer in water, reacting the water-dispersed prepolymer with a chain extender to give an aqueous urethane resin solution, and adding a curing agent to the aqueous urethane resin solution.

To obtain the urethane prepolymer, polyester polyol, diisocyanate, dimethyl propionic acid or dimethyl butyric acid, and amine are reacted. By virtue of its hydrophilicity, the dimethylpropionic acid or dimethyl butyric acid plays a role in the water dispersion of the prepolymer, later.

By way of example, and not limitation, a polyester polyol suitable for use in the preparation of the urethane prepolymer is a polybutylene adipate-based polyester polyol ranging, in molecular weight, from 500 to 3,000. If the polyester polyol has a molecular weight less than 500, the resulting film is too low in flexibility to expect good processability. On the other hand, if the polyester polyol has a molecular weight more than 3,000, the resulting film has too high flexibility

to be used for coating steel plates.

Preferably, the polyester polyol is used at an amount of 100-150 parts by weight based on the total weight of the prepolymer reactants, and more preferably
5 at an amount of 120-130 parts by weight. For example, when the polyester polyol content is less than 100 parts by weight, the resulting film is so hard that it may be peeled off while the steel plate is processed. On the other hand, when the polyester polyol content is more
10 than 150 parts by weight, the resulting film is so flexible that it may be pushed around upon processing.

The diisocyanate, which is forming a prepolymer having urethane group, is selected from the group consisting of diphenylmethane diisocyanate (MDI),
15 tolylene diisocyanate (TDI), isophorone diisocyanate (IPDI), and mixtures thereof and added at an amount of 30-50 parts by weight based on the total weight of the prepolymer reactants, and preferably at an amount of 35-40 parts by weight. For instance, when the diisocyanate
20 content is below 30 parts by weight, the backbone contains too small urethane content, so that the film lacks flexibility. Thus, upon processing, the resin is peeled off and is poor in paint adhesion. On the other hand, diisocyanate content more than 50 parts by weight
25 brings about a deterioration in general film properties, including yellowing occurrence and chemical resistance reduction.

In order to obtain a better film, the mole ratio of the diisocyanate to the polyol is so precisely calculated
30 as that a theoretical NCO % of the prepolymer is within the range of 2-8 %. In this regard, the diisocyanate may be a single compound or a mixture of two or more species.

Where the theoretical NCO residue content at the end of the backbone is below 2 % upon prepolymer polymerization, poor solution stability occurs, resulting in a decrease in film hardness. According to circumstances, the film becomes too sticky, so that its workability is poor. On the other hand, where a theoretical NCO content at the end exceeds 8 %, the film is unsuitable as coating because it becomes so brittle that peeling occurs. Thus, the maintenance of the NCO radical content within the range of 2-8 % guarantees the chain extension from the prepolymer to polyurethane resins with desired molecular weights.

Responsible for the water dispersion of the prepolymer, dimethyl propionic acid (DMPA) or dimethylbutyric acid (DMBA), which is of hydrophilicity, is used at an amount of 5-15 parts by weight based on the total weight of the prepolymer reactants and preferably at an amount of 8-10 parts by weight. Its carboxylic acid enables the prepolymer to be dispersed in water. If the hydrophilic moiety content is less than 5 parts by weight, the prepolymer is insufficiently dispersed in water so that a desired aqueous coating solution is not obtained. On the other hand, a hydrophilic moiety content more than 15 parts by weight deteriorates the corrosion resistance, chemical resistance, and paint adhesion (overcoatability) of the film.

Serving as a neutralizing agent to solubilize the prepolymer in water, amine is used at an amount of 3-10 parts by weight based on the total weight of the prepolymer reactants and more preferably at the same equivalent as that of the hydrophilic moiety.

At the reaction initiation step of the prepolymer

synthesis, amine may be added. However, since amine serves not only as neutralizing agent, but also as catalyst for the urethane reaction between ester polyol and diisocyanate, it is preferable that about 60 % of the amount to be used is added at the polymerization initiation step of the prepolymer and the remainder is fed at the termination point of the reaction before the dispersing the prepolymer in water. Available is any of primary, secondary, and tertiary amines, examples of which include n-butyl amine, diethyl amine, triethyl amine, triethanol amine, and ethylene diamine with preference to triethyl amine. In addition to possessing an excellent water solubilization potential, triethyl amine is advantageous in that since its boiling point is as low as 90 °C, it does not remain on the steel plate after coating the resin solution on the steel plate.

When amine is added at an amount less than 3 parts by weight, insufficient solubilization occurs. On the other hand, when amine is present at an amount of more than 10 parts by weight, its catalytic function is reinforced so that undesirable by-reactions may be significantly conducted.

The reactants are allowed to react with each other at 55-80 °C for about 5-6 hours with stirring to produce prepolymers which have carboxyl groups and terminal isocyan (NCO) functional groups.

On the point of the termination of the polymerization, the reaction is maintained at 30-40 °C, while water is added with stirring, so as to disperse the reaction.

When the reaction is too viscose to perform water dispersion or when it is required to facilitate the water

dispersion, a solvent such as acetone or n-methylpyrrolidone (NMP) is added at an amount of less than 10 % by weight based on the total weight of the reactants, before the water dispersion. For this, the
5 solvents may be used alone or in combination, in consideration of the physical properties of the solution. It is preferable that the solvent is added at as small an amount as possible in consideration of environment issues. When added with such a solvent, the resin solution is
10 lowered in viscosity and increased in water dispersibility and thin film coatability.

Thereafter, a chain extender is added to the water-dispersed prepolymer to synthesize aqueous polyurethane resins. The addition of the chain extender is executed
15 at the point that the reactants form a complete aqueous phase. The chain extender is fed at the same equivalent as that of the remaining NOC %. When considering that there may be a difference between the theoretical NOC % and the practical NOC %, it is preferable that 90 %
20 rather than 100 % of the amount of the chain extender is added and sufficiently reacted. A reaction sample is taken during the extension and analyzed by IR spectroscopy to determine whether the remaining amount is to be fed or not.

25 By way of example, and not limitation, the chain extender is one or two selected from glycols, such as ethylene glycol, 1,4-butylene glycol and 1,6-hexanediol, diamines, such as ethylene diamine and isophorone diamine, triols such as trimethylol propane. The reaction
30 temperature maintains 25-30°C .

The reaction temperature must be low enough not to react the NCO groups of the prepolymer to water, but high

enough to proceed the reaction.

When diols or triols are used, the reaction is preferably maintained for about 24 hours or longer because the reactivity between hydroxy (-OH) and NCO is low. On the other hand, when diamines are used, it takes about 1 hour for the reaction to be completed because of high reactivity between amine and isocyan groups. The chain extender may be selected depending on the targets where the final product is applied.

By precisely controlling the mole ratio between the NCO groups remaining in the prepolymer and the chain extender, the final molecular weight of the resin is determined. The urethane resin of this invention is determined to range, in molecular weight, from 30,000 to 100,000. A urethane resin with a molecular weight of less than 30,000 is poor in chemical resistance while a urethane resin with a molecular weight of more than 100,000 is too rapidly dried after being coated and thus, poor in coating workability. Thus, with the aid of the chain extender, there is obtained an aqueous solution of urethane resins which have a molecular weight of 30,000-100,000 and are of high chemical resistance and film coatability.

Remarkably good as it is in chemical resistance, the urethane resin solution obtained by the step(1) may be problematic when it is under an alkali condition like a degreasing process condition. In general, because resins are more vulnerable to alkali than acid, a trace of resin dissolution is found. To bring about an improvement in the chemical resistance and surface physical properties of the film, an aziridine type or block isocyan type curing agent is used at an amount of

3-15 % by weight based on the weight of the total resin solid content. For example, if the amount of the curing agent is below 3 % by weight, a desired improvement is not achieved in alkali resistance. On the other hand, if
5 the amount of the curing agent is over 15 % by weight, the film is deteriorated in paint adhesion, solution stability, surface appearance such as gloss, and processability.

To the aqueous urethane resin composition,
10 additives such as a lubricant, colloidal silica and a coupling agent are added to prepare an aqueous lubricant urethane resin composition for use in steel plates, which is superb in oil-less deep machinability, process-
defective decrease, blackening improvement, and chemical
15 resistance. This preparation is carried out at room temperature.

As for the lubricant, it is a mixture of fluorine resin-modified polyethylene type wax and polyethylene wax. When used in combination, the fluorine resin-modified
20 polyethylene type wax and the polyethylene wax bring about a greater improvement in the physical properties of the resin solution than when each is used, alone. The aqueous lubricant resin solution added with a combination
of a polyethylene type wax and a fluorine resin-modified
25 polyethylene type wax is improved in deep machinability as well as alkali resistance and solution stability.

Conventionally, a mixture of fluorine resin (PTFE)
type wax and polyethylene type wax which is prepared simply by stirring is used as lubricant. Because the
30 specific gravity of fluorine resin particles is on the order of as high as 1.6, the conventional lubricant mixture suffers from the problem of being not

homogeneously dispersed in low viscosity aqueous resin systems for thin film coating. When the conventional aqueous resin system is applied onto steel plate, the fluorine wax exists nearer the steel plate, which leads to a poor lubricating ability and an insufficient resin adhesiveness.

In contrast, the fluorine resin-modified polyethylene type wax, in which fluorine resin type wax particles are associated with polyethylene type wax particles in such a way that fine fluorine resin type wax particles are modified to surround polyethylene wax particles with significant bonding forces, has a specific gravity of 0.98-1.02, so that the aqueous lubricant urethane resin composition is improved in lubricating ability and physical properties

With reference to Fig. 1, there is shown a structure of a thin film coated on a chromated, electroplated steel plate. In the fluorine resin-modified polyethylene type wax, fluorine resin type wax particles with a diameter of 0.1-1.5 μm surround and bind to globular ethylene type wax particles which are low in specific gravity. Therefore, the fluorine resin-modified polyethylene type wax is so low in specific gravity that it has sufficient floatability even on the wetted film. In addition, the fluorine resin-modified polyethylene type wax sufficiently exerts the properties characteristic to fluorine resins by virtue of the ball bearing effect. Thus, even after being subjected to deep machining processes, the steel plate can maintain its surface clean by virtue of the fluorine resin-modified polyethylene type wax. In regard to the compatibility with aqueous solutions, the polyethylene type wax

preferably ranges, in molecular weight, from 1,500 to 3,000 with a diameter of 0.05-1.0 μm .

Because of being excellent in compatibility with and dispersability in the binder resin of the lubricant resin solution, the polyethylene type wax is homogeneously distributed in the resin film, unlike the fluorine-modified polyethylene type wax which is prevalently distributed in the upper portion of the film as shown in Fig. 1. Thus, the polyethylene type wax guarantees the uniform processability of the steel plate. In addition, its high melting point (120-130 $^{\circ}\text{C}$) maintains the wax even when the mold temperature is increased, enabling the steel plate to be continuously processed.

Preferably, the weight ratio of the fluorine resin-modified polyethylene type wax to the polyethylene type wax in the wax mixture ranges from 1:0.3 to 1:0.7. If the weight ratio of the polyethylene type wax is below 0.3 on the basis of the fluorine resin-modified polyethylene type wax, the effect of the polyethylene type wax is not sufficiently expressed so that the continuous workability becomes poor. On the other hand, if the weigh ratio is over 0.7, the physical properties of the polyethylene type wax are dominantly expressed while the deep machinability is poor.

Based on the weight of the resin solid content, the wax mixture is added at an amount of 5-30 % by weight and preferably at an amount of 10-15 % by weight. For instance, if the wax mixture is added at an amount of less than 5 % by weight, the resin solution is improved in surface friction properties to some degree, but the deep machinability is poor. On the other hand, if the

wax mixture is added at an amount of more than 30 % by weight, no additional improvements are found in the deep machinability and the resin solution suffers from the problems of being lowered in physical properties, including overcoatability and corrosion resistance.

With the aim of improving the corrosion resistance, colloidal silica is used at an amount of 10-30 % by weight based on the weight of the resin solid content. Less than 10 % by weight of colloidal silica cannot bring about a sufficient effect in the corrosion resistance. On the other hand, if the colloidal silica is present at an amount greater than 30 % by weight, silica, which is large in hardness, negatively affects the deep machinability and causes a scratchy blackening phenomenon on the processed regions.

Useful in the present invention are silane coupling agents containing epoxy, amine and/or acryl groups and titanium coupling agents containing amine groups. The coupling agents have the functions of increasing film strength so as to improve the gloss and processability of the plate as well as of uniformly dispersing the silica particles in the film so as to improve the corrosion resistance. The coupling agent is used at an amount of 0.1-0.5 % by weight based on the weight of the resin solid content.

The lubricant urethane resin composition which is prepared in consideration of practical applications can be used as functional coating resin solutions for various purposes. The solid content of the lubricant urethane resin composition may be controlled by use of pure water. For thin film coating, the lubricant urethane resin composition is diluted with pure water to a solid content

of 10-30 % by weight. If the solid content is outside of the range of 10-30 % by weight, a thin film coating is not conveniently obtained with lubricant urethane resin composition.

5 With ability to be coated on steel plates to the thickness as thin as 0.5-5.0 μm , the aqueous urethane resin composition thus obtained is superior in terms of thin film coatability, corrosion resistance, film flexibility, adhesiveness to steel plates, surface
10 friction property, chemical resistance, and overcoatability as well as in terms of compatibility with various additives which are usually used in conventional coating materials for steel plates.

As an example to which the aqueous, lubricant
15 urethane resin composition, characterized by oil-less deep machinability, process-defective reduction, blackening improvement, and chemical resistance, can be applied, there is a chromated, zinc-electroplated steel plate with a chrome deposition of 4-200 mg/m^2 . If the
20 chrome deposition is below 4 mg/m^2 , the steel plate is poor in corrosion resistance. On the other hand, when the chrome deposition exceeds 200 mg/m^2 , an excellent corrosion resistance, but a poor paint adhesion results.

The aqueous lubricant urethane resin composition
25 can be coated on electroplated steel plates in an ordinary coating method such as a roll coating method or a spray method. Preferably, the aqueous lubricant urethane resin composition is coated at a thickness from 0.5 to 5 μm when it is dried. For instance, when the
30 film thickness is below 0.5 μm , it cannot afford desired levels in film lubricating ability and workability. On the other hand, if a dry film thicker than 5 μm , no

additional improvements in processability are obtained. In addition, thick coats can be more feasibly attached to the mold upon deep machining, incurring a load to the processing process.

5 The heat provided during a baking process cures the lubricant resin of the present invention. In this regard, the baking temperature is determined within the range of 110-200 °C as the plate temperature is measured. The resin on the steel plate whose temperature is below 110
10 °C is not sufficiently cured so that it is deteriorated in chemical resistance. Also, the coat may remain undried. On the other hand, the steel plate is physically transformed at 200 °C or higher. After baking, quenching the steel plate in water.

15 A better understanding of the present invention may be obtained in light of the following examples which are set forth to illustrate, but are not to be construed to limit the present invention.

20

EXAMPLE 1

Preparation of Urethane Resin Composition

The following procedure was repeated to prepare urethane resin compositions in Examples 1-1 through 1-6
25 and Comparative Examples 1-1 through 1-12, except that amounts of each component were used as indicated in Table 1.

The following was a description of the urethane resin composition preparation set forth in Example 1-5.

30 In a reactor, 120 g of a commercially available polybutyrene adipate based polyol with a molecular weight of 2,000, 40 g of diisocyanates mixture of 2:1 by weight

ratio of diphenylmethane diisocyanate : isophorone diisocyanate, 8 g of dimethyl butyric acid, and 6 g of triethyl amine were reacted together at 65 °C for 5 hours under nitrogen atmosphere with stirring to give a
5 prepolymer with an NCO content of 3 %.

Each of the used diphenylmethanediisocyanate, isophoronediiisocyanate, dimethylbutyric acid, and triethylamine was a first grade reagent. 3 g of triethylamine was added in an initial stage of the
10 prepolymer polymerization and the remaining 3 g at a termination stage.

Thereafter, while the reactor was maintained at 35 °C, the reaction was added with 12 g of n-methylpyrrolidone and homogeneously mixed by stirring,
15 during which 284 g of distilled water was added to disperse the prepolymer.

While being maintained at 25 °C, the water-dispersed reaction was slowly added with a 8 g of 1,4-butyleneglycol, serving as a chain extender, and allowed to stand
20 for 24 hours to give an aqueous polyurethane resin solution to which an aziridine type curing agent and r-glycidoxy propyl trimethoxy silane were added at amounts of 7 % by weight and 0.2 % by weight, respectively.

Both 1,4-butyrene glycol and r-glycidoxy propyl trimethoxy silane were first grade reagents. As the
25 aziridine type curing agent, CX-100, manufactured by Zneca, was used.

After being diluted with pure water to the final solid content of 20 % by weight, the aqueous urethane
30 resin composition prepared according to the condition listed in Table 1, below, was coated on a chromated zinc-electroplated steel plate, which was 0.8 mm thick with a

zinc deposition of 20 g/m² and a chromate deposition of 50 mg/m², at a thickness of 1.5 μm with the aid of a coating simulator (bar coater) #3. Subsequently, the steel plate was baked at a temperature of 160 °C in an automatic discharging oven and quenched with water to form a film thereon.

For comparison, three types of aqueous thin film coating resins, commercially available from POSCO, Korea, were respectively applied to chromated zinc-electroplated steel plates, each being 0.8 mm thick with a zinc deposition of 20 g/m² and a chromate deposition of 50 mg/m², to form films. Epoxy acrylate was used for Comparative Example 1-13, a polyether-modified urethane resin for Comparative Example 1-14, and an ethylene acryl resin for Comparative Example 1-15. Each of the comparative resins had a solid content of 20 % by weight.

The films formed on steel plates were tested for physical properties under the following conditions:

20 <Corrosion Resistance>

Corrosion resistance was evaluated as an initial white corrosion generation time in a brine water-spraying tester in accordance with JIS Z 2731.

Corrosion Resistance Evaluation (time)

25 ◎(excellent): 120 hrs or longer, O (good): 85-100 hrs
Δ (poor): 70-85 hrs, X (bad) : less than 70 hrs

<Chemical Resistance>

1. Solvent Resistance

30 A coated surface was scrubbed 20 times back and forth with a cotton gauze soaked in methyl ethyl ketone (MEK) and the dissolution of the coat film was evaluated by the naked eye.

2. Alkali Resistance

Under the usual degreasing conditions employed in the household appliance manufacture field, a coated steel plate sample was subjected to spray degreasing and immerse degreasing, each at 60 °C for 150 sec by use of an aqueous alkali degreasing solution, washed twice with water, and air-dried, followed by measuring color differences (ΔE) before and after the degreasing with the aid of a color difference meter. Evaluation was carried out according to the following criteria:

Alkali Resistance Evaluation(ΔE)

◎ (excellent): 0.5 or less, O (good): 1.0

Δ (poor): 1.1-2.0, X (bad): 2.0 or greater.

15 <Friction Coefficient>

After being coated with a low viscosity lubricant, a sample was measured for friction coefficient at a drawing speed of 1 m/min under a pressure of 0.27 kg/cm² in an oil-less condition with the aid of a one-sided friction tester. Evaluation was performed according the following criteria:

Friction Coefficient Evaluation(μ)

◎ (excellent): 0.12 or less, O (good): 0.075-0.085,

Δ (poor): 0.085-0.095, X (bad): 0.15 or greater.

25

<Processability>

After being coated with a low viscosity lubricant, samples were subjected five times to cup molding while changing drawing ratios (DR) in a thin plate molding tester. Processability was evaluated as maximal drawing ratio values at which the cup molding was successfully achieved at least three times.

30

© (excellent): DR 1.95 or greater, O (good): DR 1.90-1.95,
Δ (poor): DR 1.90-1.80, X (bad): DR 1.80 or less

<Film Characteristics>

5 To assay the coating adhesion of the urethane
resins of Table 1 to steel plates, a thermosetting
melamine paint was sprayed over a resin-coated steel
plate to give a film 25 μm thick when it was dried,
followed by curing the film at 150 °C. After the
10 following treatments, the film was evaluated for its
characteristics.

a. Primary Adhesion: after the curing, the film was
allowed to stand for 24 hours at room temperature and
subjected to cross-cut testing under a condition of 1 mm
15 and 100 scales.

b. Water-Resistant Adhesion: after being immersed
for 30 min in boiling water, a cured sample was subjected
to cross-cut testing.

c. Adhesion after 6 mm Erichsen Processing: After
20 being cross-cut under a condition of 1 mm and 100 scales,
a cured sample was allowed to undergo a 6 mm Erichsen
processing.

d. Impact Resistance: a ball type pendulum weighing
1 kg was allowed to fall down to a cured, cross-cut
25 sample from a height 50 cm away from the sample, after
which a tape was attached to the backside of the sample
and removed to evaluate the coating adhesion.

Film Characteristics Evaluation

© (excellent): no scales, O (good): 1-2 scales
30 Δ (poor): 3-5 scales, X (bad): 6 or more scales

TABLE 1

Nos. of Examples		Resin Compositions						Properties						Notes		
		Polyol Mw	Polyol content (part)	Hydrophilic (parts)	Diisocyanate NCO (parts)	NCO %	Curing Agent (wt%)	Corrosion resistance	Films				Chemical resistance		Processability	Fric. Coeff.
									a	b	c	d				
Inventive Example	1-1	500	150	15	40	8	15 ^a	○	○	○	○	○	○	○	○	
	1-2	700	100	12	30	6	13 ^a	○	○	○	○	○	○	○	○	
	1-3	1000	130	10	50	2	10 ^a	○	○	○	○	○	○	○	○	
	1-4	1000	130	10	45	3	10 ^a	○	○	○	○	○	○	○	○	
	1-5	2000	120	8	40	3	7 ^b	○	○	○	○	○	○	○	○	
	1-6	3000	120	5	35	4	3 ^b	○	○	○	○	○	○	○	○	
Comparative Example	1-1	400	150	15	50	8	15 ^a	△	○	○	△	△	△	x	△	
	1-2	3500	110	10	30	2	5 ^a	△	○	○	△	△	○	△	△	
	1-3	1500	50	8	30	5	10 ^a	○	○	○	○	○	○	x	○	
	1-4	1500	160	10	35	3	7 ^b	○	○	○	△	△	○	x	x	
	1-5	1000	130	3	30	6	7 ^a	-	-	-	-	-	-	-	-	Impossible to make aqueous resins
	1-6	2000	120	17	40	3	10 ^a	x	○	x	△	x	x	△	○	
	1-7	1000	140	13	25	3	10 ^a	○	○	○	△	x	○	x	△	
	1-8	1000	140	13	55	3	10 ^a	△	○	△	△	△	x	△	○	Yellowing
	1-9	2000	120	10	30	1	5 ^a	○	○	○	△	x	○	x	○	Poor sol'n stability
1-10	2000	120	10	30	9	5 ^a	○	○	○	○	○	△	x	x	Too viscose	
1-11	3000	110	5	35	4	2 ^a	○	○	○	○	○	x	○	○		
1-12	3000	110	5	35	4	17 ^a	○	○	○	○	△	x	○	○	Poor sol'n stability	
1-13	Epoxy acrylate							○	○	○	○	○	△	△	○	
1-14	Polyether modified urethane							△	○	○	○	○	△	△	△	
1-15	Ethylene acrylate							○	○	○	○	○	○	△	△	

Note¹ parts or % means weight parts or weight % based on the total weight of the solid content of the final product

Note² a: blockisocyan type curing agent, b: aziridine type curing agent

Note³ a) primary adhesion, b) water-resistant adhesion, c) adhesion after 6 mm Erichsen processing, d) impact resistance

The results of Table 1 are described as follows:

Examples 1-1 to 1-6

10 Excellent physical properties were measured from the steel plate samples which were coated with the aqueous urethane resin composition prepared under the conditions of the present invention.

15 Comparative Examples 1-1 and 1-2

When the polyol used in the prepolymer polymerization has a lower molecular weight than the condition range of the present invention, a decrease is brought about in processability and chemical resistance.

20 If the molecular weight exceeds the condition range of the present invention, the film is too flexible to be suitable for use in steel plate coating.

Comparative Examples 1-3 and 1-4

25 When the content of polyol is lower than the range the present invention suggests, the film is so hard that it is peeled off while the steel plate is processed. When the polyester polyol content is more than the condition range, the film is so flexible that it is

30 pushed around upon processing. Therefore, the polyol content outside of the suggested range results in deteriorating the processability.

Comparative Examples 1-5 and 1-6

If the hydrophilic moiety content is less than the lower limit of the range the present invention suggests, the prepolymer is insufficiently dispersed in water so that a desired aqueous coating solution is not obtained.

- 5 A hydrophilic moiety content more than the upper limit of the range deteriorates general film properties, including corrosion resistance, chemical resistance, and paint adhesion.

10 Comparative Examples 1-7 and 1-8

- When the diisocyanate content is below the lower limit of the condition range of the present invention, the film lacks flexibility, which leads to a deterioration in processability, post-processing adhesion, and paint adhesion in terms of impact resistance while a diisocyanate content more than the upper limit of the condition causes yellowing and chemical resistance reduction.

20 Comparative Examples 1-9 and 1-10

- Upon prepolymer polymerization, if the theoretical content of terminal NCO residues is below the lower limit of the condition range of the present invention, not only does poor solution stability occur, but also a deterioration is brought about in processability and paint adhesion in terms of impact resistance. If a theoretical NCO content at the end exceeds the condition range, the film becomes too sticky to process the steel plate. A poor chemical resistance also results.

30

Comparative Examples 1-11 and 1-12

If the amount of the curing agent is below the

Comparative Examples 1-13 and 1-15

10 Conventional resins are poor in chemical resistance,
processability and friction properties.

Comparative Examples 1-13 and 1-15

10 Conventional resins are poor in chemical resistance,
processability and friction properties.

EXAMPLE 2

Preparation of Aqueous Lubricant Urethane Resin

15 Composition

The urethane resin solution prepared in Example 1-5 was added with a mixture of 1:1 fluorine resin-modified polyethylene wax : polyethylene wax at the amounts indicated in Table 2, below, to produce aqueous lubricant urethane resin compositions, each having a solid content of 20 wt%. As silica, Snowtex-n with a solid content of 20 % wt% (Nissin Chemical Co., Japan) was used.

25 Afterwards, the lubricant polyurethane resin compositions were coated on chromated steel plates as in Example 1 and assayed for physical properties.

<Corrosion Resistance>

Corrosion resistance was evaluated as an initial
30 white corrosion generation time in a brine water-spraying
tester in accordance with JIS Z 2731.

Corrosion Resistance Evaluation (time)

◎ (excellent): 350 hrs or longer, O (good): 300-350 hrs
Δ (poor): 250-300 hrs, X (bad): less than 250 hrs

<Chemical Resistance>

5 1. Solvent Resistance

A coated surface was scrubbed 20 times back and forth with a cotton gauze soaked in methyl ethyl ketone and the dissolution of the coat film was evaluated by the naked eye.

10 2. Alkali Resistance

Under the usual degreasing conditions employed in the household appliance manufacture field, a coated steel plate sample was subjected to spray degreasing and immerse degreasing, each at 60 °C for 150 sec by use of an aqueous alkali degreasing solution, washed twice with water, and air-dried, followed by measuring color differences (ΔE) before and after the degreasing with the aid of a color difference meter. Evaluation was carried out according to the following criteria:

20 Alkali Resistance Evaluation(ΔE)

◎(excellent): 0.5 or less, O(good): 0.6-0.8
Δ(poor): 0.9-1.5, X(bad): 1.5 or greater.

<Friction Coefficient>

25 After being coated with a low viscosity lubricant, a sample was measured for friction coefficient at a drawing speed of 1 m/min under a pressure of 0.27 kg/cm² in an oil-less condition with the aid of a one-sided friction tester. Evaluation was performed according the following criteria:

30 Friction Coefficient Evaluation(μ)

◎(excellent): 0.075 or less, O(good): 0.075-0.085,

Δ (poor): 0.085-0.095,

X(bad): 0.095 or greater.

<Deep Machinability>

A steel plate sample was subjected to plain strain
5 stretch testing (PSST) under the condition of a blank
holding force 30 tons and a punch speed 230 mm/min
without providing an oil and, then, measured for limit
dome height (LDH). The LDH value obtained before the
lubricant resin was applied, was measured to be 32-35 mm
10 as the steel plate was introduced with a low viscosity
lubricant.

Deep Machinability (mm)

© (excellent): 45 or greater,

O(good): 42-45,

Δ (poor): 38-42,

X(bad): 38 or less

15

<Appearance of Processed Surface>

After a draw bending test to determine the
occurrence of blackening in a processed surface, color
differences (ΔE) before and after the processing with the
20 aid of a color difference meter. Evaluation was carried
out according to the following criteria:

Appearance of Processed Surface

© (excellent): 0.5 or less, O(good): 0.5-2.0

Δ (poor): 2.0-4.0,

X(bad): 4.0 or greater.

25

TABLE 2

Nos. of Exmpl.		Composition (wt%)		Properties					Notes
		Lubricant	Silica	Corrosion resistance	Chemical resistance	Fric. Coeff.	Deep Machinability	Appearance	
Inventive Example	2-1	5	10	○	○	○	○	○	
	2-2	5	20	◎	○	○	○	○	
	2-3	10	10	○	◎	◎	○	◎	
	2-4	10	15	○	◎	◎	◎	○	
	2-5	15	20	◎	◎	◎	◎	◎	
	2-6	20	20	◎	○	◎	◎	◎	
	2-7	20	30	◎	◎	◎	◎	◎	
	2-8	25	30	◎	◎	◎	◎	○	
	2-9	30	35	◎	◎	◎	◎	○	
Comparative Example	2-1	3	15	○	△	x	x	x	
	2-2	32	20	△	○	◎	◎	◎	
	2-3	35	20	△	△	◎	◎	◎	
	2-4	20	5	△	◎	◎	◎	◎	
	2-5	20	40	◎	◎	△	x	x	Scratching

As indicated in Table 2, the steel plates coated with the lubricant resin solutions prepared according to the present invention are excellent in all of the physical properties tested. In contrast, when lubricant resin solutions contain smaller lubricant contents than suggested by the present invention, the steel plates are generally poor in processability. When lubricant resin solutions contain larger lubricant contents than suggested by the present invention, far from being improved in processability, the steel plates become poor in corrosion resistance. A silica content lower than the desired range results in deteriorating the corrosion resistance while a higher silica content incurs blackening and scratching upon processing because silica has a large hardness. In the latter case, the steel plates show poor deep machine, as well.

In this example, measurements were measured of the effect of the weight ratio of polyethylene wax to fluorine resin-modified polyethylene wax on the physical properties of the steel plate.

5 Aqueous lubricant urethane resin solutions were prepared as indicated in Table 3. The polyethylene wax used was one purchased from Daedong, Korea, identified as PS-35, which has a solid content of 26 wt%. The
10 fluorine-modified polyethylene wax was 25 wt% in solid content and commercially available. Each of the aqueous lubricant resin solutions was applied to the resin composition prepared in Example 5-2. The aqueous
15 lubricant urethane resin compositions thus obtained were tested for deep machinability and post-processing appearance as in Example 2.

TABLE 3

Nos. of Exmpl.		Wt Ratio of PE wax*	Properties		Notes
			Deep Machinability	Post-Process. Appearance	
Comparative Example	3-1	0	△	○	
	3-2	0.1	△	○	
	3-3	0.2	△	○	
Inventive Example	3-1	0.3	○	◎	
	3-2	0.4	○	◎	
	3-3	0.5	◎	◎	
	3-4	0.6	◎	◎	
	3-5	0.7	○	○	
Comparative Example	3-4	0.8	△	△	Poor Sol'n Stability

* weight ratio of polyethylene wax to fluorine resin-modified polyethylene wax

20

As recognized from Table 3, a mixture of fluorine resin-modified polyethylene wax and polyethylene wax which is within the weight ratio range of the present invention enhances the deep machinability and post-
25 processing appearance of the steel plate fluorine.

Resin-modified polyethylene wax alone or a wax mixture containing a polyethylene wax at a lower content than suggested by the present invention does not give a desirable contribution to the machinability of the steel plate. In the case of a larger content of polyethylene wax than suggested, the effect attributed to fluorine resin-modified polyethylene wax is not expressed.

As described hereinbefore, the aqueous lubricant urethane resin composition for thin film coating prepared according to the present invention is superior in various physical properties, including corrosion resistance, paint adhesion, chemical resistance, processability, and surface friction properties and suitable as a binder resin for coating functional steel plates. A lubricant coating solution containing the aqueous urethane resin, when applied as a thin film to a steel plate, gives a great contribution to improving the steel plate in corrosion resistance, chemical resistance, deep machinability, post-processing appearance, and surface friction properties as well as enables the steel plate to be processed into products under an oil-less condition. This oil-less condition results in omitting a degreasing process, thereby bringing about a favor economically and environmentally.

The present invention has been described in an illustrative manner, and it is to be understood that the terminology used is intended to be in the nature of description rather than of limitation. Many modifications and variations of the present invention are possible in light of the above teachings. Therefore, it is to be understood that within the scope of the appended claims,

the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A method for preparing an aqueous urethane resin composition, comprising the steps of:

- 5 (1) producing an aqueous polyurethane resin solution by
- (a) reacting 100-150 parts by weight polyester polyol, 30-50 parts by weight diisocyanate, 5-15 parts by weight dimethyl propionic acid or
- 10 dimethyl butyric acid, and 3-10 parts by weight amine at 55-85 °C for 5-6 hours to give a prepolymer ranging, in NCO radical content, from 2 to 8%, said dimethyl propionic acid or
- dimethyl butyric acid serving as a hydrophilic moiety for water dispersion;
- 15 (b) dispersing the prepolymer at 30-40 °C in water; and
- (c) introducing into the water-dispersed prepolymer a chain extender selected from the
- 20 group consisting of glycol, triol and diamine at 25-30 °C in such a way that the reaction mole ratio between said chain extender and NCO residues is controlled to give the final
- product with a molecular weight of 30,000-
- 25 100,000;
- (2) adding the aqueous polyurethane resin solution with block isocyan type or aziridine type curing agent at an amount of 3-15 % by weight based on the weight of the resin solid content.

30

2. A method for preparing an aqueous lubricant urethane resin composition, comprising the steps of:

(1) producing an aqueous polyurethane resin solution by

5 (a) reacting 100-150 parts by weight polyester polyol, 30-50 parts by weight diisocyanate, 5-15 parts by weight dimethyl propionic acid or dimethyl butyric acid, and 3-10 parts by weight amine at 55-85 °C for 5-6 hours to give prepolymer ranging, in NCO radical content, from 2 to 8%, said dimethyl propionic acid or
10 dimethyl butyric acid serving as a hydrophilic moiety for water dispersion;

(b) dispersing the prepolymer at 30-40 °C in water; and

15 (c) introducing into the water-dispersed prepolymer chain extender selected from the group consisting of glycol, triol and diamine at 25-30 °C in such a way that the reaction mole ratio between said chain extender and NCO residues is controlled to give the final
20 product with a molecular weight of 30,000-100,000;

(2) adding the aqueous polyurethane resin solution with block isocyan type or an azidirine type curing agent at an amount of 3-15 % by weight
25 based on the weight of the resin solid content;

(3) adding a mixture comprising a fluorine resin-modified polyethylene and a polyethylene wax at a ratio of 1:0.3-1:0.7 to the resin solution at an amount of 5-30 % by weight based on the weight of
30 the resin solid content, said fluorine resin-modified polyethylene wax ranging, in specific gravity, from 0.98 to 1.02 with a particle size of

0.1-1.5 μm , said polyethylene wax ranging, in molecular weight, from 1,500 to 3,000 with a particle size of 0.05-1.0 μm ;

5 (4) adding a colloidal silica in the resin solution obtained in the step (3) at an amount of 10-30 % by weight based on the weight of resin solid content;

10 (5) adding in the resin solution obtained in the step (4) a coupling agent selected from the group consisting of silane coupling agents containing an epoxy group, an amine group, and/or an acryl group and titanium coupling agents containing phosphorus and/or an amine group at an amount of 0.1-0.5 % by weight based on the total weight of the resin solid content; and

15 (6) diluting the resin solution with pure water into a final resin solid content of 10-30 % by weight.

20 3. The method as set forth in claim 1 or 2, wherein said polyester polyol is used at an amount of 120-130 parts by weight based on the weight of the prepolymer reactants.

25 4. The method as set forth in claim 1 or 2, wherein said diisocyanate is used at an amount of 35-40 parts by weight based on the weight of the prepolymer reactants.

30 5. The method as set forth in claim 1 or 2, wherein said hydrophilic moiety for water dispersion is used at an amount of 8-10 parts by weight based on the weight of the prepolymer reactants.

6. The method as set forth in claim 2, wherein said wax mixture is used at an amount of 10-15 parts by weight based on the weight of the prepolymer reactants.

5

7. The method as set forth in claim 1 or 2, further comprising the step of adding acetone and/or n-pyrrolidone solvent at an amount 10 % by weight based on the weight of the prepolymer reactants, before the
10 dispersing step.

8. The method as set forth in claim 1 or 2, wherein said polyol is a polybutylene adipate based polyester polyol with a molecular weight of 500-3,000.

15

9. The method as set forth in claim 1 or 2, wherein said diisocyanate is selected from the group consisting of diphenylmethane diisocyanate, isophorone diisocyanate, and tolylene diisocyanate.

20

10. The method as set forth in claim 1 or 2, wherein said amine is triethyl amine.

11. The method as set forth in claim 1 or 2,
25 wherein said chain extender is selected from the group consisting of glycols, such as ethylene glycol, 1,4-butylene glycol, and 1,6-hexane diol, diamines, such as ethylene diamine and isophorone diamine, triols such as trimethylol propane, and mixtures thereof.

30

13. A surface treatment of chromated, electroplated steel plates, comprising the steps of: coating, on an

zinc-electroplated steel plate chromated at a chrome amount of 4-200 mg/m², the aqueous lubricant urethane resin at a dry coating thickness of 0.5-5.0 μm, baking the steel plate at a steel temperature of 110-200 °C, and
5 quenching the steel in water.

10

15

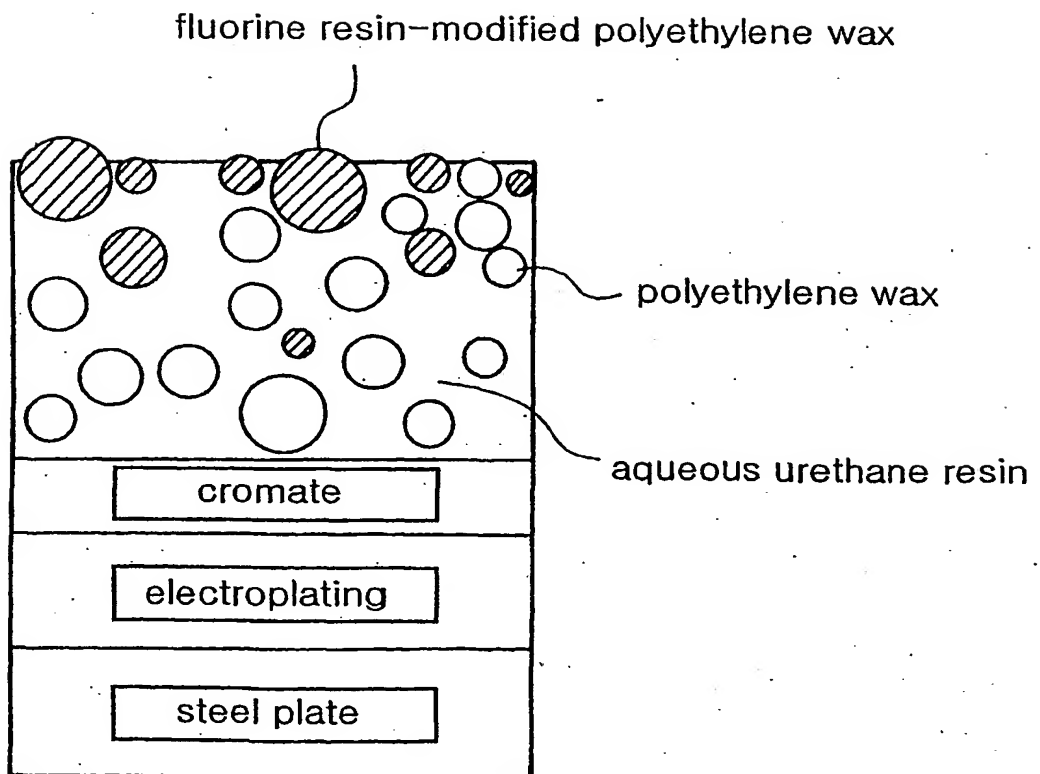
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1/1

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 00/00657

CLASSIFICATION OF SUBJECT MATTER

IPC⁷: C08G 18/66, 18/10, 18/34, B05D 7/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁷: C08G 18/00, B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, PAJ, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 4301053 A (WOLFREY A.A.) 17 November 1981 (17.11.81) claims 1,7.	1-5,7,12
A	EP 0884336 A1 (BASF AKTIENGESELLSCHAFT) 16 December 1998 (16.12.98) claims, page 3, lines 47-58, page 6, lines 3-6.	1-5,7-9,11,12
A	US 5569707 A (BLUM H. et al.) 29 October 1996 (29.10.96) claims 1, 11, column 6, lines 1-14, example 1.	1-5,7-9,11,12

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

„A“ document defining the general state of the art which is not considered to be of particular relevance

„E“ earlier application or patent but published on or after the international filing date

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„O“ document referring to an oral disclosure, use, exhibition or other means

„P“ document published prior to the international filing date but later than the priority date claimed

„T“ later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

„X“ document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

„Y“ document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

„&“ document member of the same patent family

Date of the actual completion of the international search

9 March 2001 (09.03.2001)

Date of mailing of the international search report

30 March 2001 (30.03.2001)

Name and mailing address of the ISA/AT

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR 00/00657

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 11 138096 A (NIPPON STEEL CORP.) 25 May 1999 (25.05.99) (abstract). [Online retrieved on 2001-03-09]. Retrieved from EPO PAJ Database.	1,2,6,12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 00/00657

REMARK:

Claim 13 has been renumbered to claim 12, because only 12 claims have been transmitted.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR 00/00657

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